UNDERGROUND MINING ENGINEERING 27 (2015) 41-48 UDK 62
UNIVERSITY OF BELGRADE - FACULTY OF MINING AND GEOLOGY YU ISSN 03542904

Original scientific paper

SOME CONTRIBUTIONS TO THE EXAMINATION OF COMPOSITES FROM POWER PLANT WASTES

DOPRINOS PROUČAVANJU KOMPOZITA NAPRAVLJENOG OD OTPADNIH MATERIJALA TERMOELEKTRANA

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Received: September 17, 2015 **Accepted:** October 15, 2015

Abstract: This paper describes an investigation into the possibilities of the use of all three types of solid power plant wastes: fly ash (FA), flue gas desulphurization gypsum (FGD gypsum) and bottom ash (BA) as components of composites for road construction. Two mixtures were made: 1. power plant wastes - Portland cement (PC) and 2. power plant wastes - sand (S) - Portland cement (PC). The mass ratio of components in these mixtures was:

1. FA - FGD gypsum - BA - PC = 2 : 1.5 : 5 : 1.5 and
2. FA - FGD gypsum - BA - S - PC = 2 : 1.5 : 4 : 1 : 1.5.

For both mixtures, the compressive strength, the mineralogical composition, the water absorption and the resistance to freeze-thaw treatment were determined 7 and 28 days after preparation of samples (mixing with water). The obtained results showed that both mixtures could have potential to be used for sub-base layers in road construction and the second mixture (with natural aggregate-sand) has advantage over the first mixture in terms of compressive strength, mineralogical composition, and resistance to freeze-thaw treatment.

Key words: fly-ash, bottom ash, flue gas desulphurization gypsum, road construction

Apstrakt: Ovaj rad istražuje mogućnosti korišćenja sva tri tipa čvrstog otpadnog materijala termoelektrana: letećeg pepela (FA), sulfogipsa (FGD gips) i šljake (BA) kao komponenti za izradu kompozita koji će se koristiti za izradu podloge puteva. Ispitivane su dve smeše: 1. otpadni materijal termoelektrana-Portland cement (PC) i 2. otpadni materijal termoelektrana-pesak (S) i Portland cement (PC). Maseni odnos komponenti u smešama bio je:

1. FA - FGD gips - BA - PC = 2 : 1.5 : 5 : 1.5 i
2. FA - FGD gips - BA - S - PC = 2 : 1.5 : 4 : 1 : 1.5.

Za obe mešavine, ispitivane su pritisna čvrstoća, minerološki sastav, apsorpcija vode i otpornost na niske temperature posle 7 i 28 dana, nakon pripremanja uzoraka (mešanja sa vodom). Dobijeni rezultati su pokazali da obe mešavine imaju potencijalnu mogućnost upotrebe za donje noseće slojeve kolovoznih konstrukcija puteva, pri čemu je druga mešavina (sa prirodnim agregatom-peskom) u prednosti u odnosu na prvu mešavinu u pogledu pritisne čvrstoće, minerološkog sastava i otpornosti na tretman smrzavanje/odmrzavanje.

Ključne reči: elektrofilterski pepeo, šljaka, sulfogips, izrada puteva

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1. INTRODUCTION

The thermal power plants produce three types of solid wastes (fly ash - FA, flue gas desulphurization gypsum - FGD gypsum and bottom ash - BA). The disposal of these wastes is an economic and an ecological problem (pollution of air, waters and soil). Consequently, their utilisation in bulk (as materials for road construction) is of great importance.

The application of wastes from power plants as materials for road construction is connected with their characteristics. FA with low CaO content (the class F according to ASTM 618) may exhibit pozzolanic properties and could be applied as a substitute for Portland cement (PC) in concrete (Manz, 1999; Benavidez et al. 2003; McCarthy and Dhir, 1999; Freidin and Motzafi-Haller, 1999; Asokan et al. 2005).

BA is a more or less inert material, i.e., bottom ash usually does not exhibit pozzolanic properties, but it could be a potential aggregate in concrete as a replacement for natural sand (its particles are coarse, sized between sand and gravel, fused and with a glassy texture) (Benavidez et al. 2003; Cheriaf et al. 1999; Bai and Basheer, 2003).

FGD gypsum could be applied as a chemical activator of FA in FA/cement systems, based on the ability of gypsum to react with aluminium oxide in the glass phase of fly ash to produce ettringite that contributes to the strength in the early ages (Poon et al. 2001).

The aim of this work was to broaden the knowledge concerning the applicability of power plant wastes as components in cement based composites for road construction FA and BA, applied in this work, originated from Serbian power plant "Nikola Tesla" and FGD gypsum from Bohemian Power Plant - Hvaletice (no Serbian plant has a FGD system installed yet).

2. EXPERIMENT

2.1. Materials

The following materials were used:

- Portland cement (PC) with 32.80% CaO and 45.72% SO_3 contents;
- Fly ash of the class F according to ASTM 618 ($SiO_2 + Al_2O_3 + Fe_2O_3 = 80.66\%$) and its mineralogical composition (presence of typical crystalline phases: quartz, mullite, anhydrite, feldspar, diopside, gehlenite and hematite, as well as presence of amorphous phase). Its physical properties were: fine sand and silt sized particles (lower than 0.208 mm), density 2.088 g/cm^3 and bulk density 0.7970 g/cm^3;
- Bottom ash (BA) with lower oxides content ($SiO_2 + Al_2O_3 + Fe_2O_3 = 61.42\%$) and mineralogical composition: quartz, calcite, anhydrite, feldspar, diopside and hematite (presence of amorphous phase in it was lower than in fly ash). Physical properties of bottom ash were: sand-gravel sized particles (0.208 mm to 4.699 mm), density 1.9670 g/cm^3, bulk density 0.5377 g/cm^3 and maximum dry density 0.7490 g/cm^3;

- Flue gas desulphurization gypsum (FGD gypsum) containing 96.55% $CaSO_4 \cdot 2H_2O$, composed of fine sand-silt sized particles (96.66 % lower than 0.074 mm), with density of 2.3400 g/cm^3 and bulk density of 1.3590 g/cm^3;
- Sand (S) with the maximum grain size of 2 mm;
- Tap water (W).

2.2. Proportions and methods of examination of mixtures

Two kinds of the mixtures (pastes) were made: the first was composed of power plant wastes (FA, FGD gypsum, BA), Portland cement (PC) and water (W) and the second contained sand (S) in addition to the mentioned components in the first mixture.

To simulate the stabilization (necessary for use of the mixtures in road construction), cylindrical specimens (diameter 10.2 cm and height 11.7 cm), so-called Proctor specimens, were made by the standard Proctor compaction procedure (ASTM D698). The necessary quantity of water applied for preparation of these specimens presented the content of water at which the mixtures became most dense and achieve their maximum dry density (so called the optimum moisture contents - OMC).

The content of components in solid phase and the content of water (OMC) in the mixtures are given in Table 1.

Table 1 - Composition of mixtures

Mixture designation	**Content of components in solid phase [%]**					**Content of water (OMC) [%]**[*]
	FA	**FGD gypsum**	**BA**	**S**	**PC**	
M_1	20	15	50	-	15	36.533
M_2	20	15	40	10	15	35.211

[*] water is given in % of mass of solid components

Twelve Proctor specimens of both mixtures were stored for 7days and the another twelve of both mixtures were stored for 28 days in a humid room (20°C ± 2°C, 85% humidity). After storage, the following properties of the specimens were determined: compressive strength, mineralogical composition, water content, absorption of water and resistance to freeze-thaw cycling.

The compressive strength was determined according to the Serbian Standard SRPS U.B1.030 (which is in accordance with the European Standard EN 14227-4). The values of compressive strength presented herein are average value of the compressive strength of three specimens of both hardening mixtures after 7 and 28 days. For an assessment of the validity of the results of compressive strength, they were compared with the criteria for compressive strength of sub-base layers proposed by Public Enterprise-Roads of Serbia.

The mineralogical compositions of pulverized and crushed specimens (during the determination of their compressive strength) were determined by the powder XRD technique using the Philips PW 1729 X-ray generator and the Philips PW 1710 diffractometer. The obtained XRD-diffractograms of samples were interpreted by means of JCPDS cards. Also, XRD-diffractograms were used to estimate the development of obtained products (phases) of the hydration reactions during period from 7 to 28 days. Namely, the peak intensities (I in cps) of products after 28 days (I_{28}) and after 7 days (I_7) were read from X-ray difractograms and than the ratios I_{28} / I_7 were calculated. The ratio $I_{28} / I_7 < 1$ signified a diminution and ratio $I_{28} / I_7 > 1$ signified augment of content of phases (products).

Water content and absorption of water of monolithic (non-crushed) cylindrical (Proctor) specimens were determined as the average value of three specimens after 7 and 28 days, according to SRPS U.B1.012 and SRPS B.B8.010, respectively.

The resistance to freeze-thaw cycling of monolithic (non-crushed) cylindrical (Proctor) specimens was determined using the durability test procedure specified in SRBS U.B1.050 (as an average value of three specimens after 7 and 28 days). This freeze-thaw procedure is correlated to the mass loss and volume change after 14 freeze-thaw cycles.

3. RESULTS AND DISCUSSION

3.1. Compressive strength

The results of the compressive strength determinations of the specimen S_1 (made from mixture M_1 in Table 1) and the specimen S_2 (made from mixture M_2 in Table 1) after 7 and 28 days are presented in Table 2. The estimated standard deviations for the compressive strength are also given in Table 2.

Table 2 - Compressive strength results for hardened specimens

Specimen	Compressive strength [MPa]		Standard deviation [MPa]	
	7 days	28 days	7 days	28 days
S_1	1.6804	3.4854	0.1626	0.0741
S_2	1.8749	3.7442	0.0254	0.0185

The specimen S_2 (in which 20 mass % of bottom ash was substituted with sand) had greater compressive strength values than the specimen S_1 (in which sand was not present), both after 7 and 28 days of hardening (by 11.57% and 7.42%, respectively). These results are probably connected with the higher porosity and inferior physical properties (density, bulk density, maximum dry density) of bottom ash compare to those of sand.

Table 3 - Compressive strength
of cement-stabilized mixtures or sub-base layers

Layer	Compressive strength [MPa]	
	7 days	28 days
Sub-base for motor ways and very heavy traffic load	2 - 5.5	3.0 - 6
Sub-base for heavy and medium traffic load	1.5 - 5.5	2.5 - 6

The criteria for compressive strength of subbase layers proposed by the Public Enterprise-Roads of Serbia are presented in Table 3.

Comparing the obtained results (Table 2) with the criteria in Table 3, it could be concluded that both mixtures prepared in this work are suitable as the sub-base for heavy and medium traffic load.

3.2. XRD analysis

Based on the results of the XRD analysis (interpreted by JCPDS cards) it could be stated that both specimens (S_1 and S_2) contained the same crystalline phases: quartz, mullite, ettringite, gypsum and calcite, as well as the amorphous phase of C-S-H.

Quartz and mullite detected in the specimens, were inherent to fly ash and bottom ash.

Ettringite and C-S-H were the products of the hydration reactions that occurred. Ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) was formed by the reaction between calcium aluminate, from Portland cement and FA, and gypsum from FGD gypsum and Portland cement (Holly et al. 2006):

$$3CaO \cdot Al_2O_3 + 3CaSO_4 \cdot 2H_2O + 26H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \quad (1)$$

C-S-H (hydrated calcium silicate) was the product of the reactions between tricalcium silicate (C_3S) and dicalcium silicate (C_2S), from Portland cement, and water, according to:

$$\text{Portland cement}\left(C_3S, C_2S\right) + H_2O \rightarrow \text{C-S-H} + Ca\left(OH\right)_2 \quad (2)$$

Because $Ca(OH)_2$ was not present in the specimens (stated by X-ray diffraction analysis) it could be concluded that the liberated $Ca(OH)_2$ (2) reacted with active silicates from fly ash (present in the amorphous phase of FA) to form also calcium silicate hydrate (C-S-H).

The presence of gypsum and calcite in both specimens (S_1 and S_2) could be interpreted and explained by means of the ratios of the intensities of the XRD peaks (I_{28} / I_7) of these phases. The ratios of the intensities (in cps) of the XRD peaks of ettringite, gypsum and calcite for the specimens after 28 and 7 days (calculated on the basis of their values read from XRD diffractrograms of the specimens) are presented in Table 4.

Table 4 - The ratios of the intensities of the XRD peaks of the specimens after 28 and 7 days

Specimen	**Ratio of intensities of XRD peaks (I_{28} / I_7)* (peak intensity after 28 days/peak intensity after 7 days)**		
	Ettringite $d = 0.9730$ nm ($2\theta = 9.16^{\circ}$)**	**Gypsum $d = 0.7630$ nm** ($2\theta = 11.59^{\circ}$)**	**Calcite $d = 0.3035$ nm** ($2\theta = 29.40^{\circ}$)**
S_1	0.58	1.32	1.52
S_2	1.70	0.68	1.05

* ratio < 1 signifies a diminution and ratio > 1 signifies augment of content of phases

** these peaks were chosen because they did not overlap with those of other phases

Based on the results presented in Table 4, the following development of the phases during the hydration reactions (from 7 to 28 days) were stated:

- The diminishing of the content of ettringite ($I_{28} / I_7 = 0.58$) and the augment of the contents of gypsum ($I_{28} / I_7 = 1.32$) and calcite ($I_{28} / I_7 = 1.52$) in the specimen S_1;
- The augment of the content of ettringite ($I_{28} / I_7 = 1.70$), the diminishing of the content of gypsum ($I_{28} / I_7 = 0.68$) and practically the same content of calcite ($I_{28} / I_7 = 1.05$) in the specimen S_2.

The diminishing of the content of ettringite as well as the augment of the contents of gypsum and calcite could be related to the carbonation phenomenon which occurred in the specimen S_1, via reactions with atmospheric CO_2, according to the equations (Garcia-Gonzales et al. 2006; Chen et al. 2007; Fernández Bertos et al. 2004):

$$\begin{aligned} &3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O + 3CO_2 \rightarrow \\ &\rightarrow 3CaCO_3 + 3CaSO_4 \cdot 2H_2O + Al_2O_3 \cdot nH_2O(gel) + (26\text{-}n)H_2O \end{aligned} \tag{3}$$

$$CxSHy + zCO_2 \rightarrow Cx - zHy + zCaCO_3 \tag{4}$$

Because the contents of gypsum and calcite were not increased while the content of ettringite was in the specimen S_2, it could be concluded that the carbonation phenomenon is not occurred in this specimen.

The obtained results could be consequence of the fact that the diffusivity of CO_2 (and therefore the carbonation) depends of the porosity of a solid - low porosity inhibits the diffusion of CO_2 into the solid (Fernández Bertos et al. 2004). The substitution of 20 mass % of porous BA with non-porous sand in S_2 probably diminished the diffusion of CO_2, which was a possible reason that carbonation did not occur in this specimen.

3.3. Water content and absorption of water

The water content and the absorption of water of monolithic (non-crushed) cylindrical (Proctor) specimens after 7 and 28 days are presented in Table 5.

Table 5 - Water content and absorption of water of the specimens

Specimen	Water content [%]		Absorption of water [%]	
	after 7 days	after 28 days	after 7 days	after 28 days
S_1	35.09	40.99	35.59	30.41
S_2	32.66	32.25	32.66	32.33

The increase of water content and the decrease of absorption of water in the Specimen 1 from 7 to 28 days (Table 1) could be related to the carbonation phenomenon which took place during mentioned period in the specimen. It seems that ettringite decomposition with the release of a lot of water (3) caused the increase of water content and that calcite formation (4) caused the decrease of absorption of water, because of calcite which was deposited in pore volume of material during carbonation (Valls and Vàzquez, 2001; Johannesson and Utgenannt, 2001).

The obtained results (presented in Table 4), which suggested that practically no differences in water content and absorption of water between 7 and 28 days for S_2 specimen, are very probably connected with the fact that the carbonation phenomenon did not occur in the Specimen 2.

3.4. Freeze–thaw resistance

The results of the freeze-thaw resistance are given in Table 6.

Table 6 - The mass loss and volume change of the specimens

Specimen	Mass loss [%]		Volume change [%]	
	after 7 days	after 28 days	after 7 days	after 28 days
S_1	1.01	1.74	0.85	1.56
S_2	1.51	0.95	1.34	1.51

The criteria of SRPS U.B1.050 standard are: the maximum of 14% of mass loss and the maximum of 2% of volume change after 14 freeze-thaw cycles. On this way both specimens (S_1 and S_2) had satisfactory freeze-thaw resistance, after 7 days and 28 days as well (Table 6).

Moreover, it is evident from Table 6 that the specimen S_2 (composed of FA, PC, FGD gypsum, BA and S) after 28 days exhibited the highest freeze-thaw resistance.

4. CONCLUSION

Based on aforementioned it could be concluded the following:

1. Both mixtures:
   FA - FGD gypsum - BA - PC - W (2 : 1.5 : 5 : 1.5, *MOC* = 36.533%) and
   FA - FGD gypsum - BA - S - PC - W (2 : 1.5 : 4 : 1 : 1.5, *MOC* = 35.211%),
   satisfied the criteria for sub-base layers, regarding the compressive strength values (proposed by the Public Enterprise-Roads of Serbia) and the freeze–thaw resistance (SRPS U.B1.050).
2. The examinations performed in this work indicated that carbonation reactions occurred in the mixture without sand (the first mixture). The products of these reactions could have both positive role (formed $CaCO_3$ can improve structural properties of material), and negative role (formed gypsum may cause delayed ettringite formation and eventually cracking of material). Consequently, long-term examination (longer than 28 days) should be included in future investigations.

ACKNOWLEDGEMENT

This paper was realized as a part of the project "Study of Possibilities for Valorization of the remaining Coal Reserves to Provide Stability of the Energy Sector of Republic of Serbia" (TR 33029) financed by the Ministry of Education, Science and Technological Development of the Republic of Serbia within the framework of Programme of research in the field of technological development for the period 2011-2015.

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